Tracing metals and comparing BC sources in atmospheric aerosols samples collected at UALR

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Summer 2009
US Department of Energy
GCEP-SURE program
UALR – Department of Chemistry

Outline

- Background : Atmospheric aerosols
- TXRF Spectroscopy
- Measuring black carbon (BC) concentration in the atmosphere and its dependence on weather conditions.
- Future work
- Aknowledgements

Atmospheric aerosols physical and chemical properties

- Aerosols are suspension in a gas, usually air, of microscopic liquid or solid particles, such as smoke, dust, fog, or smog, that tend to remain dispersed rather than to settle.

- They help in the formation of cloud droplets acting as cloud condensation nuclei.

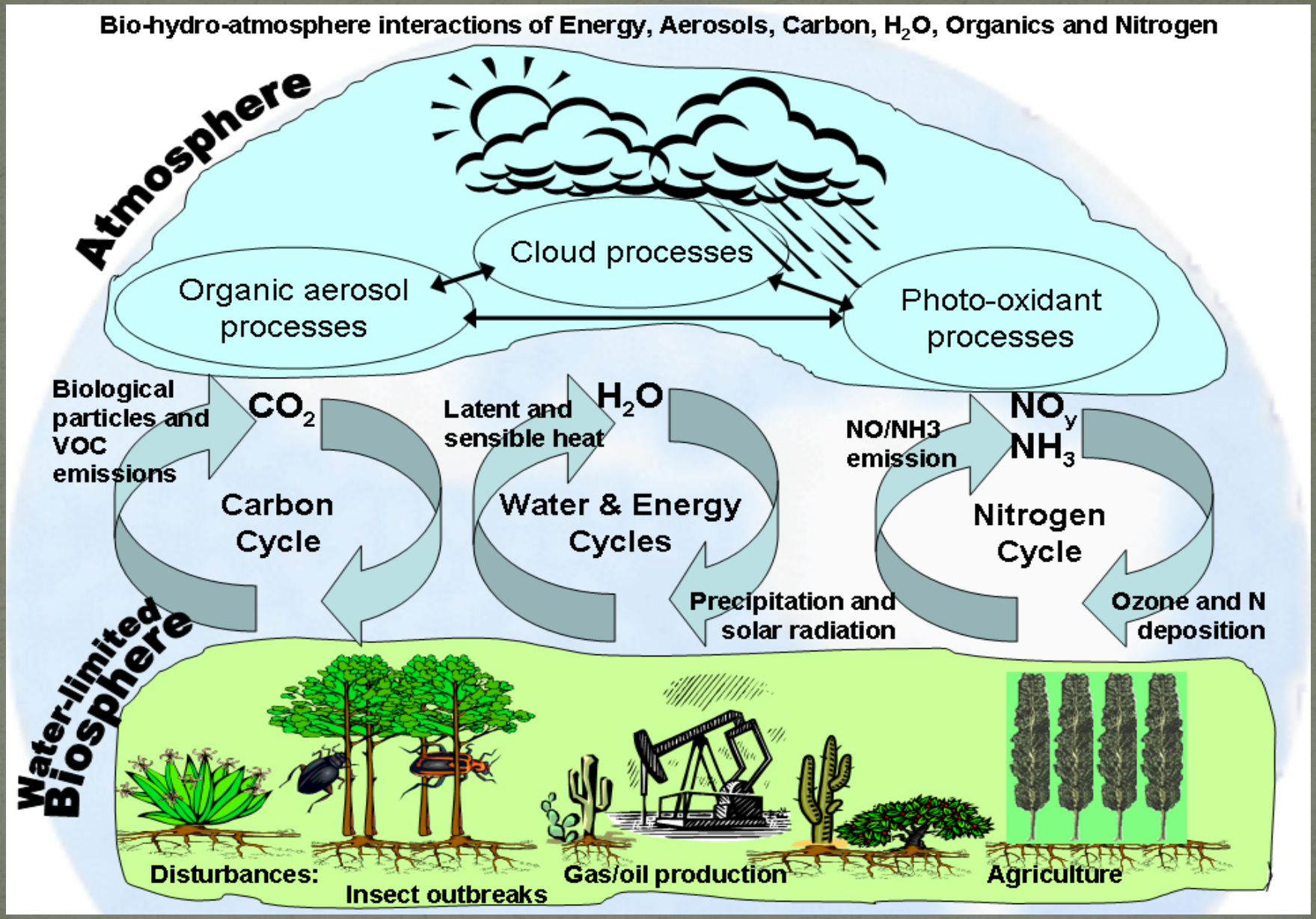
- More aerosol in the atmosphere equals smaller water droplets in clouds (average size 20 microns) which reflects more solar radiation back to space.

Atmospheric aerosols physical and chemical properties

- Scattering is primarily dependent on particle size.
  - Ex. Sulfate aerosols which cooling effect in the N Hemisphere is comparable in magnitude to the atmospheric warming produced from increases in CO_2 .
- Absorption is largely dependent upon chemical composition.
  - Ex. BC aerosols produced from incomplete combustion can reduce the amount of sunlight reaching the Earth's surface by as much as 10% .
  - However, they can also increase the solar energy absorbed in the atmosphere by as much as 50% (dominant absorber) leading to significant local warming of the boundary layer.

Atmospheric aerosols physical and chemical properties

- Other light absorbing carbonaceous species that are present in atmospheric aerosols are:
  - Aromatic hydrocarbons – produced along with BC during combustion
  - Nitrated derivatives – formed by atmospheric oxidation in the presence of NO_2.
  - Amino acids – biological particles
  - Polycarboxylic acids known as “humic-like” substances (HULIS) – produced by biomass burning, atmospheric oxidation of BC or atmospheric oxidation of biogenic hydrocarbons



2007 ESSL Annual Report - NCAR

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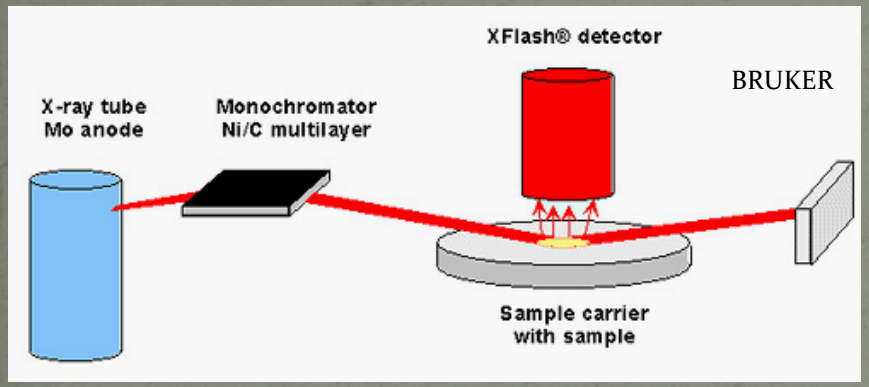
Total X-Ray Fluorescence Spectroscopy

- Bruker's TXRF S2 PICOFOX is a portable bench-top instrument that is useful for quantitative and semi-quantitative multi-element microanalysis of liquids, solids or powders.
  - The principle used for such analysis is called total reflection X-ray fluorescence spectroscopy (or TXRF spectroscopy).
  - This instrument can be used to trace metals in atmospheric aerosols samples collected in a filter media.

BRUKER

TXRF Spectroscopy

Description of principle:



- The primary beam is generated by a X-ray tube.
- The X-ray spectrum depends on the anode material which in this case is molybdenum .
- This beam is monochromatized by Bragg-reflection on a multilayer.
- Then these X-rays hit a sample carrier under a very small angle of incidence.
- The X-rays are totally reflected by the surface of the sample carrier and fluorescence radiation is emitted by the sample substance.
- From this we get a spectrum for the sample (see next slide).

*Sample carrier is either a quartz glass disk or an acrylic glass disk.

PICOFOX

File Edit View Project Spectrum Device Measurement Analyze Export User Window ?

Live Time: 1000 s | 01_blank_psap_1@260809_094622 | Unknown sample

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01_blank_psap_1@260809_094622

psap_blanks_082509.rtx

- Project
  - Information
  - Objects
    - Job
    - Spectra
      - 01_blank_psap_1
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      - 02_blank_psap_2
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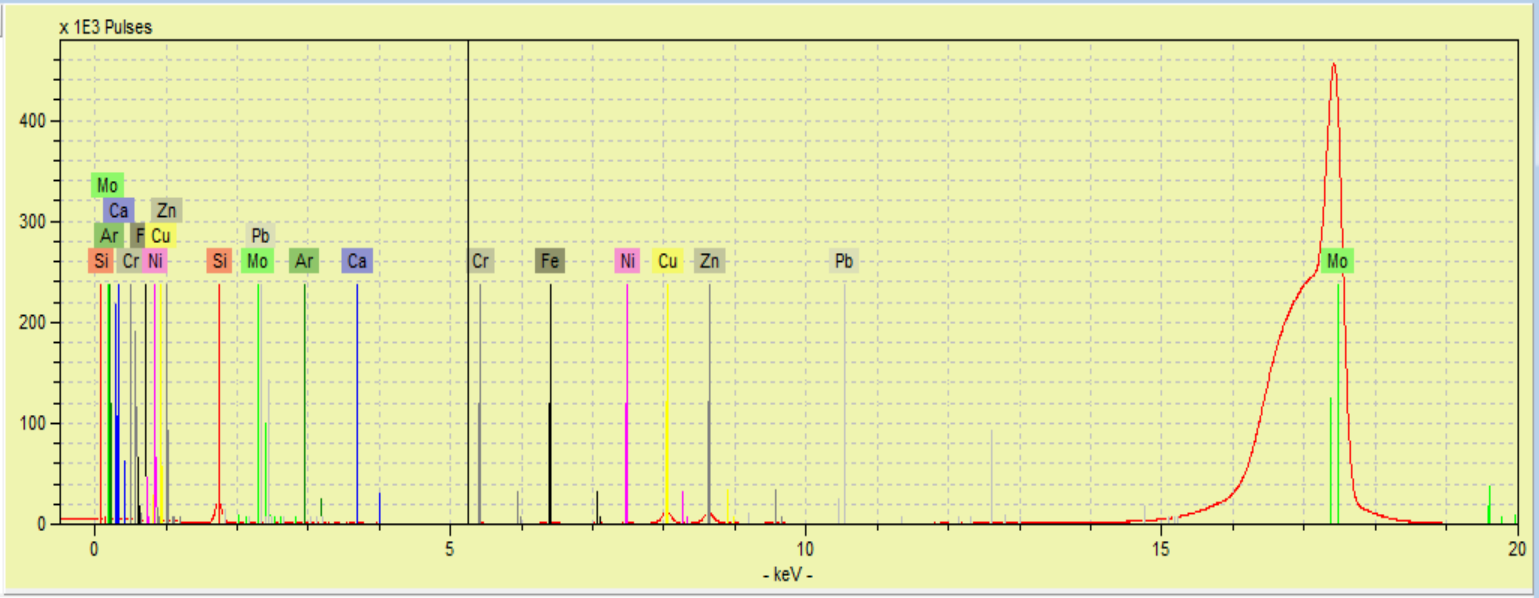

Results - 01_blank_psap_1@260809_094622

Method: Unknown sample

Corrections
- Escape: Yes
- Shelf: No
- Background: Yes
- Cycles: 200

Identification
- Method: Line markers

Deconvolution
- Method: Super bayes (normal fit)
- Max. cycles:
- Step width:

Quantification
- Calculate: Yes
- Cal. file: PICOFOX_Mo_Wind River

No.	Element	Line	Energy/keV	Cycl.	Net	Backgr.	Sigma	Chi	Conc./%	SigmaC/%	LLD/%
1	Si	K12	1.740	200	460174	67144	771	36.00			
2	Ar	K12	2.958	200	1002	46639	307	1.49			
3	Ca	K12	3.692	200	5421	44915	309	0.92	4.975	0.283	0.583
4	Cr	K12	5.415	200	4497	47594	316	1.09	1.363	0.096	0.198
5	Fe	K12	6.405	200	40927	50881	378	2.28	8.024	0.074	0.133
6	Ni	K12	7.480	200	7761	54216	341	1.43	1.047	0.046	0.094
7	Cu	K12	8.046	200	386474	55370	705	12.15	46.416	0.085	0.085
8	Zn	K12	8.637	200	362978	57044	691	21.57	37.506	0.071	0.074
9	Mo	K12	17.480	200	56941776	383747	7597	63747.12			
10	Mo	L1	2.292	200	2145	53735	331	1.94			
11	Pb	L1	10.551	200	6546	57789	349	0.89	0.669	0.036	0.074
12	Pb	M1	2.342	200	1	52519	324	2.59			

E: Cnts: OFFLINE

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TXRF PICOFOX

- All elements present in the sample are identified using the periodic table as shown in figure 1. The concentration can be obtain either in ppm or %.
- The series lines fitted for each element are shown in figure 2.
- Some advantages of this instruments are:
  - Data and/or graphic can be easily exported to an excel sheet for further analysis.
  - Sample amounts needed for study are in the nanogram to microgram range.
  - Low operating cost.

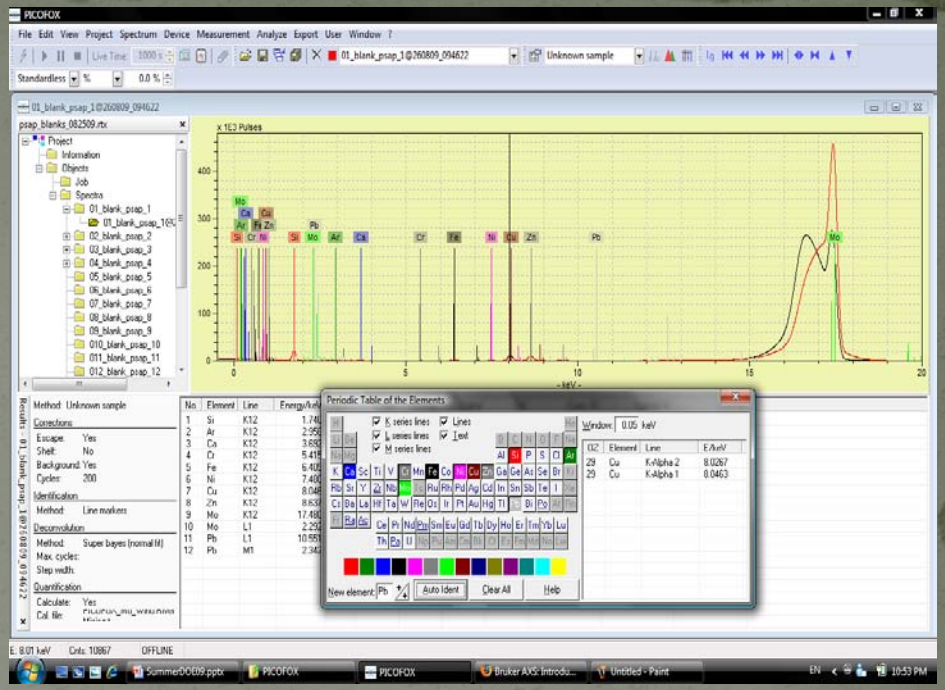

Figure 1

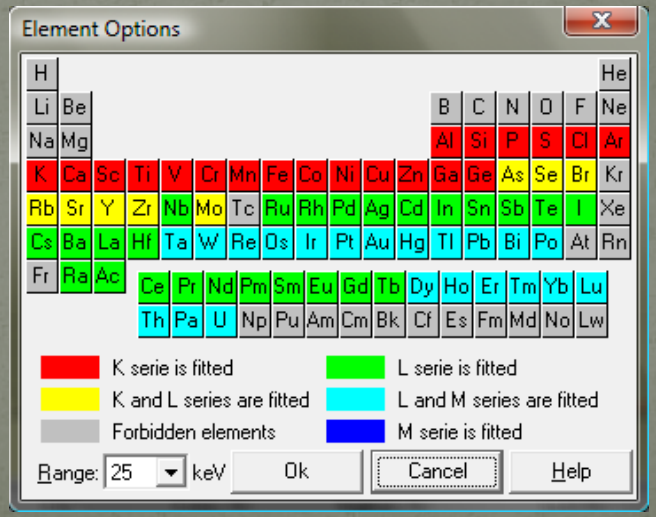

Figure 2

Outline

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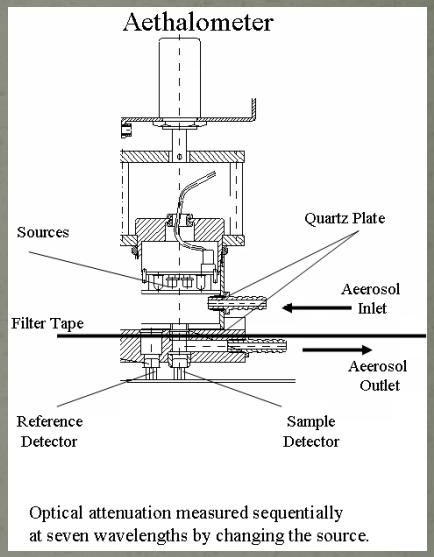
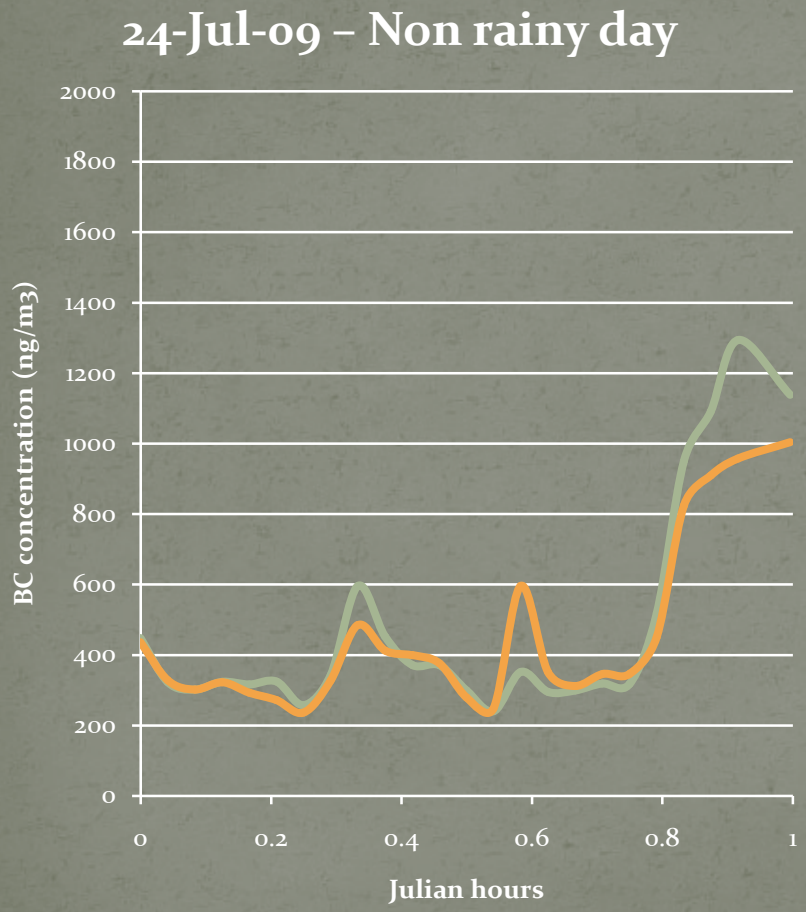
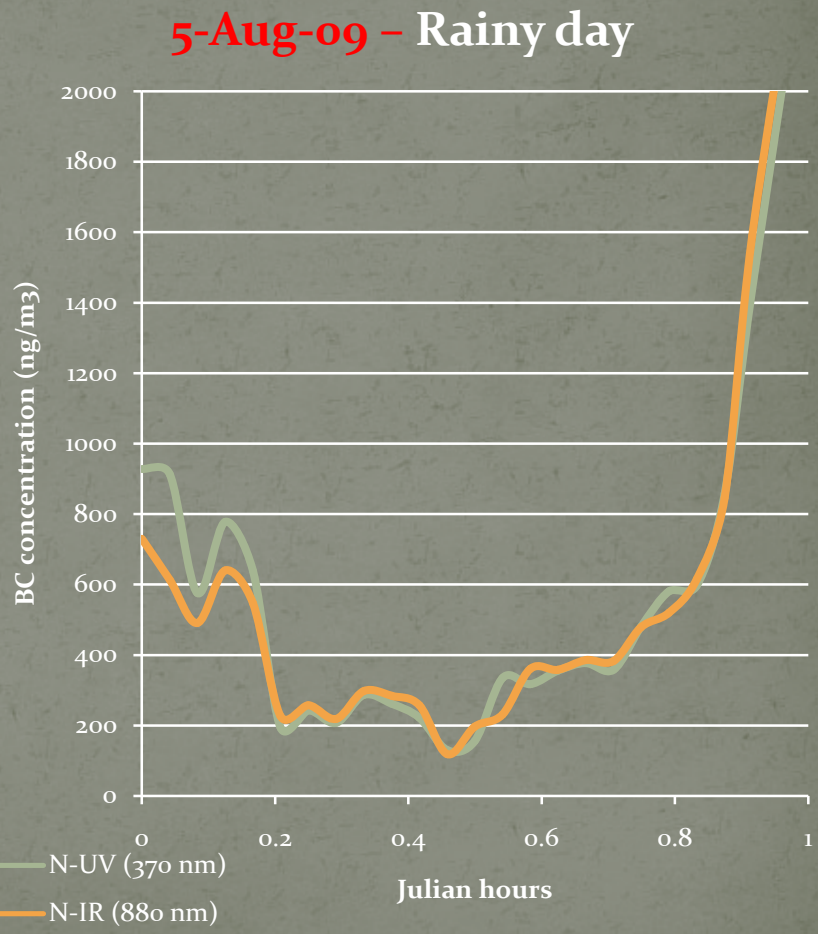
Aethalometer

- The aethalometer is a tape sampler that takes in air at a controlled flow rate, and then passes the air through a special glass fiber filter tape.
- Black carbon is measured using optical absorption at a near-IR source wavelength (880 nm).
- An additional second wavelength source is available in the near-UV (370nm)
- These two wavelengths can be used to compare emissions due to low combustion efficiency versus engine deterioration and for providing further information about different potential sources of BC.

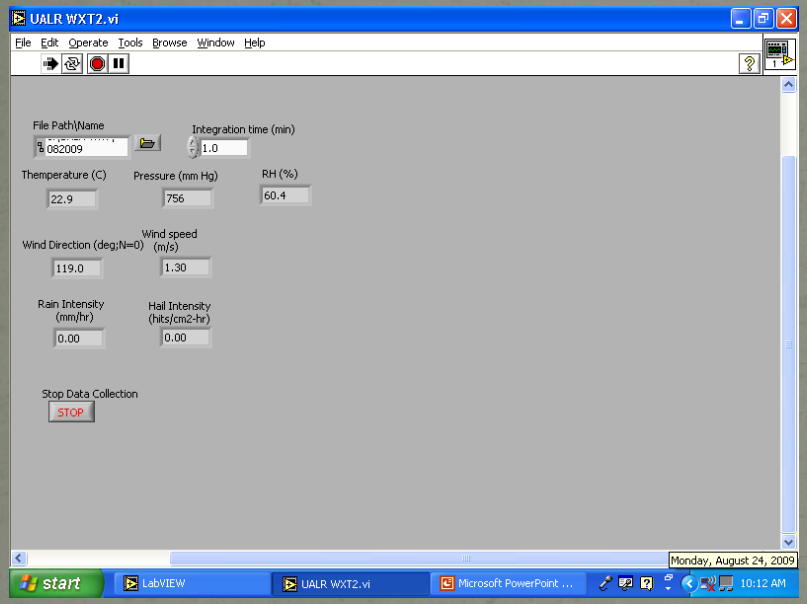


Aethalometer : Ex. UALR Near UV vs Near IR BC concentration measurements





Weather data collection



- WXT 510 is an instrument designed to measure various weather parameters like wind speed and direction, RH, temperature, pressure, rain intensity and hail intensity.

- Also a rain gauge is used to collect water samples during rain events.

Conclusion

- TXRF Spectroscopy
  - This type of spectroscopy has proven to be very useful to trace metals in bulk samples like the atmospheric aerosols collected in filter media.
  - Also it provides the concentration in the sample of each of those metals which is very useful for characterization of compounds in the sample.
- Black carbon sources
  - Studying BC concentration variation in a day using the near UV (370 nm) and N-IR (880 nm) wavelengths seems to be a good way of characterizing BC concentration diurnal cycle and see the trends during rain and non-rain events.

Future work

- TXRF Spectroscopy
  - Run all samples available for further analysis using trace metals.
- Black carbon vs DOC concentrations
  - Study black carbon concentrations and dissolved organic carbon concentration in rain water during rain events at UALR.
  - Also correlating this amounts to weather variables such as temperature, boundary layer mixing, relative humidity and wind.

Acknowledgments

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